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FIELD EXPERIENCE WITH AMBIENT-LEVEL FLAME-PHOTOMETRIC SULPHUR DETECTORS*

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Summary—Carbon dioxide exhaled by the operators produces increased levels of this gas inside the trailers used for housing monitoring equipment for use in the field. These levels can be high enough to produce serious calibration errors in flame photometric detectors used for measuring ambient concentrations of gaseous sulphur products. Quantitative measurement of the carbon dioxide interference in the sulphur emission is reported, as well as a method of estimating the extent of quenching agent pollution.

A field programme is in progress in Montana conducted by the Environmental Protection Agency (EPA) to identify and measure the environmental effect of coal-fired power plants. Part of it is devoted to monitoring air-quality several miles downwind from the Colstrip power plants in a rather remote area of the state. Four monitoring stations with different degrees of instrumentation have been established downwind in the most prevalent direction of air-mass flow. They are located in semi-arid rangeland with access essentially limited to 4-wheel drive vehicles. Each station basically consists of a small trailer which serves to provide shelter and a controlled environment for the instruments. Three of them are completely self-contained, generating and regulating their own power systems. Each is equipped with a sulphur analyser for continuous monitoring of the atmosphere. At present these analysers are all flame photometric devices (FPD). This report covers experiments conducted at our major monitoring location (Hay Coulee). Here we have gained experience with several manufacturers' instruments as well as various analytical monitoring techniques for atmospheric sulphur determination.

In a major effort to improve the accuracy of the data being collected under sponsorship of the EPA, an independent contractor (Rockwell International) has been assigned the task of ensuring quality and routinely inspects and tests all equipment utilized for data collection in programmes operated by or for this Federal agency. The results of these routine audits are used to suggest methods of improving accuracy and defining the limits of error for a particular batch of data. In general, this system has fulfilled its purpose. We have been responsible for operation of the Colstrip (Montana) stations during the past year, and have found unexplained differences between the Rockwell calibrations of the sulphur monitors and ours, even though standard NBS permeation tube calibration sources and other accepted dilution techniques were presumably used throughout. This paper is a report of the magnitude and cause of these errors, of conditions conducive to their occurrence, and of their elimination.

Extensive use has been made of the flame spectrometric method for the determination of sulphur-containing compounds.[1,2] It is based on the light emitted from the excited S_2 band in a hydrogen-rich flame. The emission is highly dependent on the nature and temperature of the flame. Precise gas-metering and mixing make high accuracy and reproducibility attainable. The effect of other gaseous substances on the molecular emission of the S_2 species has been reported,[3,4] that of organic compounds and carbon dioxide being a decrease in response. The interference is a function of the concentration of the compounds concerned, but is often independent of the sulphur-compound level.[5]

At the Hay Coulee site it was noted from time to time that unexplained zero shifts would occur when the internal trailer air was used as the carrier-gas. These shifts were not constant from day to day. Small zero shift effects which may not have been observed or considered important by other workers were critical to the validity of our monitoring data since all values measured in the clean environment were below 50 ppM (parts per milliard)†. For this reason we made

*This work was performed for the U.S. Environmental Protection Agency under Interagency Agreement EPA-IAG-D7-0473.

† All concentrations are expressed as v/v.

it a practice always to use ambient air from outside the trailer as the primary source of "zero" air, and it was always passed through appropriate clean-up beds. At the time of the last audit we noted that air from inside the trailer was being used as the carrier-gas. It seemed reasonable to assume that interfering materials which were not scrubbed from the carrier gas might be causing the discrepancies. Although the temperature within the trailers was controlled for the benefit of the instruments, there was no provision for ventilation with air from outside. Indeed some effort had been made in the past to reduce draughts on account of the harsh climate. The most obvious cause of flame interference was increased atmospheric concentrations of carbon dioxide from human breath, and the effect would be greater on audit days when 3 or 4 adults would be present.

EXPERIMENTAL

To examine and measure the effects of changes in CO_2 concentration in the carrier-gas on sulphur response, an experimental arrangement for gas-mixture control was built. This consisted of a supply of pure CO_2 gas fed into a double-dilution air system. The dilution air was passed through "Ascarite" to remove CO_2. Standardized concentrations of CO_2 in air could then be prepared, including the range typical of normal air. This mixture was purified over silica gel and charcoal before entering an SO_2 permeation system calibrated by NBS. The response to changing mixtures of SO_2 and CO_2 was measured in a standard FPD sulphur analyser.* This instrument was initially calibrated with normal outside air and an SO_2 permeation tube. In this manner, deviations in SO_2 response, caused by changes in CO_2 concentration, could be observed and related to the auditing problems. Four concentrations of SO_2 gas were used, in the range 20—100 ppM. At each concentration, the sulphur emission intensity was observed when 4 standard carbon dioxide mixtures and normal outside air were used in turn as carrier gas compositions of these mixtures were chosen to include the CO_2 concentrations to be expected under such confined conditions. A series of similar experiments was conducted with a second ambient-air monitor.† Both monitors were utilized on this project for sulphur analysis.

DISCUSSION

The results of carbon dioxide interference in the sulphur emission are shown as a log–log plot in Fig. 1. Included for comparison is the effect of carrier air containing the CO_2 concentration produced during a typical day with two adult workers inside the trailer. It is apparent that the slopes of these curves are essentially constant. That is, the interference with the emission is independent of the concentration of the sulphur dioxide. This is in agreement with the findings of Sugiyama *et al.* for other quenching agents.[5]

A plot of the instrumental response to low concentrations of SO_2 in the presence of varying CO_2 levels is shown in Fig. 2. The response is expressed as net photomultiplier tube (PMT) current in nA, which is

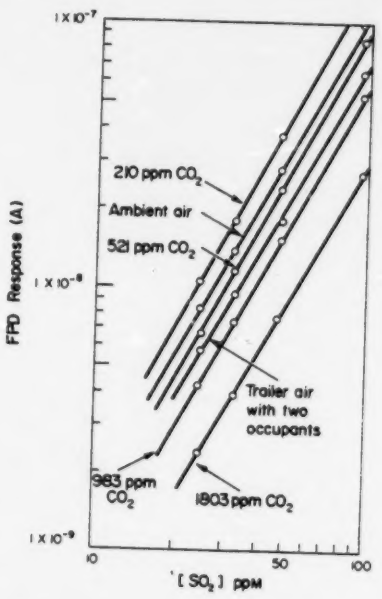

Fig. 1. Quenching of low-level sulphur emission by CO_2.

the same as the percentage shown on the 1E − 7 scale of the Meloy SA160 analyser. The net PMT current is computed by subtracting from the gross PMT current the dark current and the current obtained for "zero air". Extrapolation of the instrumental output to higher concentrations of carbon dioxide indicates that the sulphur response should be completely quenched by about 3000 ppm of CO_2. The slopes of the curves are a function of the SO_2 levels. Figure 3 is a curve generated by log–log regression analysis, illustrating the empirical relationship between changing instrumental response and changing interference level. The slope of the carbon dioxide vs. response curve may be expressed as a function of the SO_2 levels.

$$\frac{\Delta \ln[CO_2]}{\Delta \text{response}} = f[SO_2] \tag{1}$$

where $[CO_2]$ and $[SO_2]$ are expressed in ppm and ppM respectively. This curve is the basis of an empirical relationship showing how the analyser response varies as the CO_2 level changes.

The curve was analysed with respect to the actual variations produced by changes in SO_2 level. It was found that

$$f[SO_2] = K[SO_2]^x \tag{2}$$

where K and x are -140 and -2.0, respectively, and therefore the change in instrumental output is

$$\Delta \text{response} = \frac{\Delta \ln[CO_2]}{-140[SO_2]^{-2.0}}. \tag{3}$$

*Meloy Laboratories Model SA 160.
† Meloy Laboratories Model 285E.

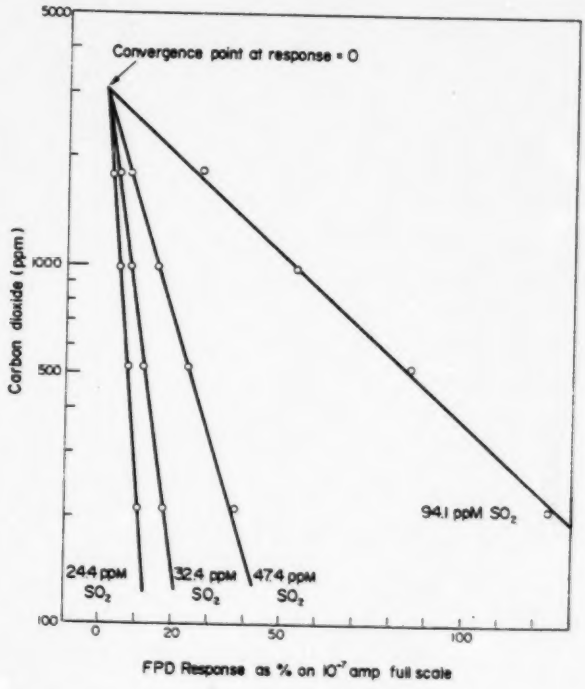

Fig. 2. Effect of CO_2 on FPD response to varying $[SO_2]$.

Therefore:

$$\Delta(\text{response}) = \frac{(\ln[CO_2]_{final} - \ln[CO_2]_{initial})[SO_2]^{2.0}}{-140} \quad (4)$$

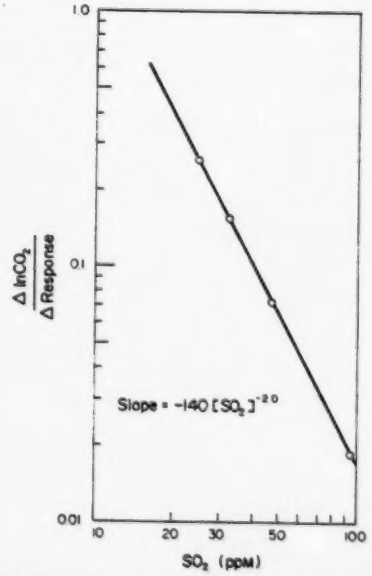

Fig. 3. Relationship between CO_2 concentration, FPD response and SO_2 concentration.

The standard deviations for K and x were derived from 3 regression lines. The relative standard deviations were 18.9% for K and 0.04% for x. It is apparent that increasing concentrations of CO_2 will decrease the response. Equation (4) can then be used to predict the response from the expected changes in carbon dioxide level and observations on standards. By using the response changes from Fig. 1 for particular concentrations of sulphur dioxide and substituting into equation (4) we can also calculate the level of CO_2 present when the trailer had two occupants. This was found to be 750 ppm.

Other estimates can be made of the carbon dioxide concentration within the trailer when it is occupied. The respiratory rate for a man in light activity is about 1200 litres of air per hr, with an oxygen to carbon dioxide conversion of about 4%.[6] The net carbon dioxide input is, therefore, 48 l./man-hr and thus 96 l./hr when two men are present. Our trailer volume is approximately 40,000 litres of which 13.2 will be CO_2 under standard conditions. Assuming that sufficient time had elapsed for CO_2 equilibrium to have been achieved, then the value of 750 ppm measured represents the resultant input from the two occupants. This net carbon dioxide gain of 17 l./hr is the resultant of the production rate (96 l./hr) and the loss-rate from the trailer. The rate of carbon dioxide loss is, therefore, 79 l./hr. If we assume that complete mixing occurs between the incoming air containing 330 ppm of carbon dioxide and the polluted air before escape

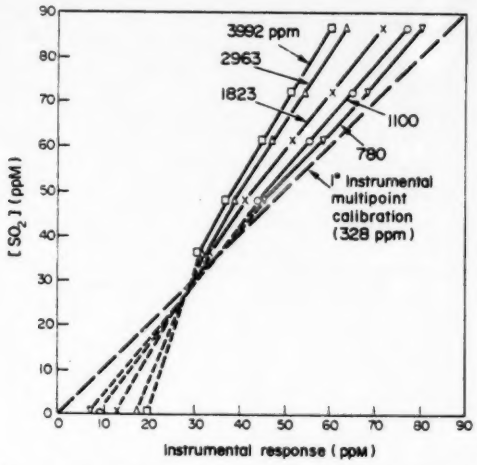

Fig. 4. Interfering effects of CO_2 on the SO_2 response of a Meloy 285E ambient sulphur analyser.

of the latter, then some 2.7 air-changes occur per hour within the trailer. Less complete mixing would allow the observed carbon dioxide concentrations with less air turnover. From this, the carbon dioxide concentrations to be expected from additional occupants can be estimated. From human respiration rates, it is apparent that without some ventilation the 8-hr exposure limit of 5000 ppm (American Institute of Industrial Hygiene) could be exceeded within the trailer during an 8-hr day.

Experimental results from testing of the second type of instrument were sufficiently different from those for the first to be of interest. In this case, lower interference levels were observed in the presence of CO_2; however, certain peculiarities were manifest. Figure 4 illustrates the change in sulphur response with varying CO_2 concentrations. Both positive and negative effects were observed when elevated CO_2 levels were present, when the results were compared with those obtained with instruments calibrated to operate in air containing ambient CO_2 concentrations. The combination of the various effects produced a fortuitously correct response in the region of about 30 ppM SO_2. At higher SO_2 levels, increasing concentrations of CO_2 provide more quenching of the sulphur emission. This is in agreement with the observations in our first case study. At lower levels of SO_2, unexpectedly high instrumental responses were obtained, which increased with increasing CO_2 concentration. Discussions with the manufacturer suggest this to be the result of instrumental bias built in to minimize the effect of changing CO_2 concentrations upon the response curve. This analyser is adjustable to cope with almost any background CO_2 level (by means of the zero offset control, which is usually set by the factory for the normal ambient CO_2 concentration of about 330 ppm).

Obviously, analysts must be on guard concerning the possibility of build-up of carbon dioxide or organic material in the carrier air. This can result not only from respiration, but from many other sources, including natural features (swamps, biota), factories (downwind from chimney stacks), fire *etc.* It is important either to be aware of the effect of changing concentrations of interfering components present, or to make measurements after calibration under the conditions to be used for the tests themselves.

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